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Preparation and pH dependent reversible color change of (hexafluoroacetylacetonato)bis(ethylenediamine)chromium(III) complex

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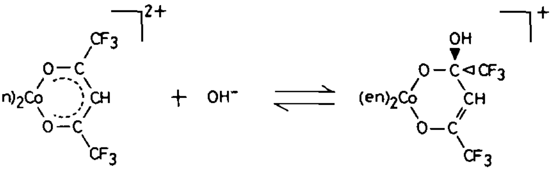
Abstract

The title complex ion was newly prepared as a hexafluorophosphate perchlorate salt. The aqueous solution of this complex shows a pH dependent, rapid and reversible color change. This phenomenon is analogous to that observed for its Co(III) analog and may be explained by a hydroxide ion addition equilibrium to the coordinating hexafluoroacetylacetonato ligand. The estimated equilibrium constant is significantly larger than that for its Co(III) analog.

Introduction

A decade ago, one of the authors prepared a complex salt $[Co(en)_2(hfac)](ClO_4)_2$ and found a unique hydrolysis of this complex (Hhfac = hexafluoroacetylacetone) [1]. The color of an aqueous solution of this complex changes rapidly and reversibly with variation of pH value of the solution; orange in acid and violet in base. In later NMR and X-ray studies, this color change has been ascribed to a reversible hydroxide addition to one of the carbonyl carbon atoms of the hfac ligand [2–4].



We are further interested in the corresponding hydrolysis in the case of the Cr(III) analog. In this work, we report the preparation of $[Cr(en)_2(hfac)](PF_6)(ClO_4)$ and the pH dependent reversible color change of this complex in water.

Experimental

cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O$ (2.37 g; 8 mmol) was dissolved in warm water (2 ml) [5]. When the solution became reddish, 6 M $HClO_4$ (2 ml) was added and warmed further for several minutes (M = mol dm^{-3}). This solution was neutralized by addition of 3 M NaOH (4 ml) and combined with an aqueous solution containing Hhfac (8 mmol) and NaOH (8 mmol). The resultant mixture was maintained at 45 °C for 1 h and insoluble precipitates were removed by filtration. Drops of 3 M NaOH were added to the red–violet filtrate until the color turned to blue–violet. Violet needle crystals were obtained on addition of $NaClO_4$ (2 g) and were recrystallized from water by addition of $NaClO_4$. This violet product (1.9 g) was dissolved in 6 M $HClO_4$ (5 ml). After addition of NH_4PF_6 (1.2 g) and $NaClO_4$ (1.2 g), the solution was ice cooled. The resultant orange colored crystals were collected by filtration, recrystallized from acetone and washed by ethanol–ether (1:9) mixture. Yield 0.5 g. *Anal.* Found: C, 17.2; H, 2.7; N, 9.2. Calc. for $[Cr(en)_2(hfac)](PF_6)(ClO_4)$: C, 17.3; H, 2.8; N, 9.0%.

Results and discussion

When an orange colored complex salt $[Cr(en)_2(hfac)](PF_6)(ClO_4)$ is dissolved in water, an orange colored solution is formed. If one adds a dilute aqueous solution of NaOH to this solution, its color immediately changes to blue–violet. By a successive addition of $HClO_4$, the color returns to the original one. The absorption spectra are shown in Fig. 1. In acidic solution, two absorption peaks exist at 21 050 ($\epsilon = 94$) and 28 820 (4466) cm^{-1}. These can be assigned to a d → d transition of the Cr(III) center and the t_{2g}(metal) → π^*(ligand) charge transfer transition in agreement with similar transitions for $Co(en)_2(hfac)^{2+}$: 20 530 (139) and 28 570 (2500) cm^{-1} [1]. Compared with the corresponding transitions 20 200 (96) and 29 940 (6290) cm^{-1} for $Cr(en)_2$-

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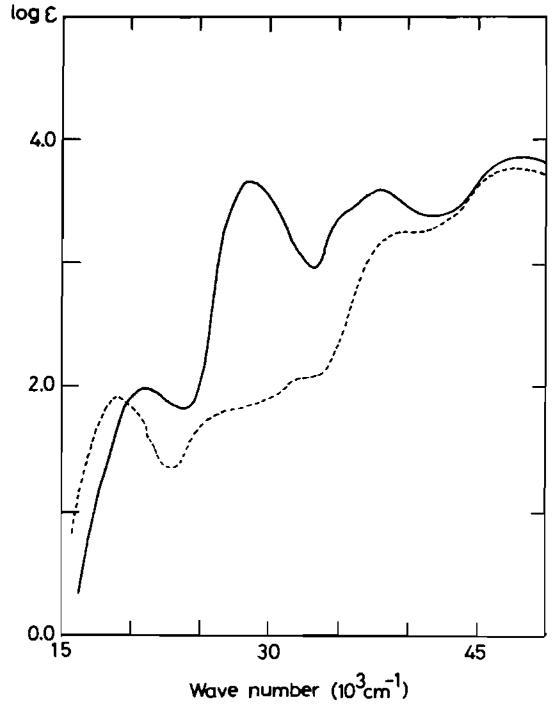


Fig. 1. Absorption spectra of $[Cr(en)_2(hfac)](PF_6)(ClO_4)$ in water. Optical path length = 1 cm; —— $[HClO_4] = 50$ mM; ----- $[NaOH] = 50$ mM.

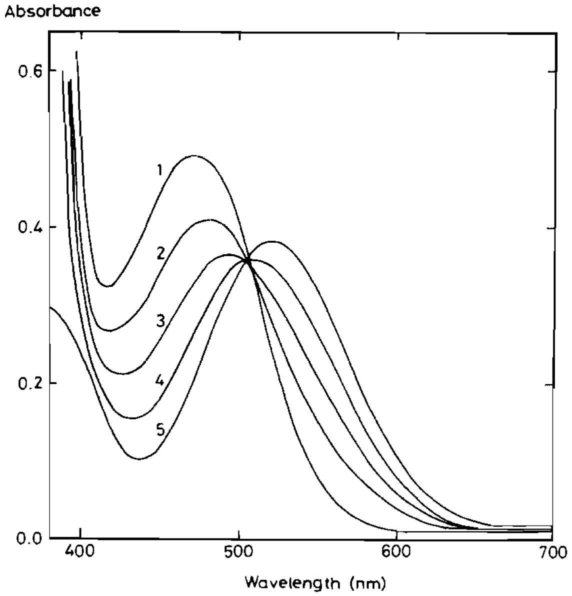
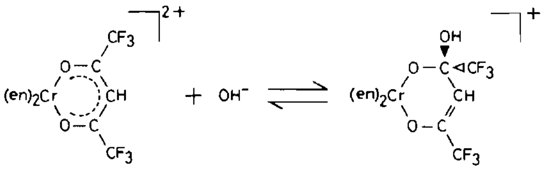


Fig. 2. pH dependent variation of the absorption spectrum of $Cr(en)_2(hfac)^{2+}$ in water at 15 °C. Total concentration of the Cr(III) complexes is 5 mM. 1, $[HClO_4] = 50$ mM; 2, $[NaOH] = 1.25$ mM (pH = 2.94); 3, $[NaOH] = 2.50$ mM (pH = 3.39); 4, $[NaOH] = 3.75$ mM (pH = 3.82); 5, $[NaOH] = 50$ mM.

$(acac)^{2+}$, the first band of $Cr(en)_2(hfac)^{2+}$ lies at higher energy demonstrating the stronger crystal field of a hfac ligand than an acac ligand (Hacac = acetylacetone) [6]. In basic solution, the first band shifts significantly to lower energy and exists at 19 230 (77) cm^{-1} and the charge transfer band vanishes. This spectral change is analogous to that observed in the case of $Co(en)_2(hfac)^{2+}$: in basic aqueous solution, the first band shifts to 19 120 (130) cm^{-1} and the charge transfer band vanishes [1]. Disappearance of the charge transfer band in basic solution suggests that a drastic change occurs in the degree of delocalization of the π electron system of the hfac ligand. Therefore one can ascribe this pH dependent spectral change of $Cr(en)_2(hfac)^{2+}$ to a reversible σ bond formation of a hydroxide ion to one of the carbonyl carbon atoms of the hfac ligand.



In Fig. 2, absorption spectra at several pH values are shown. The isosbestic point at 505 nm supports the existence of only two complex species in these solutions. The concentration ratio of the two complex species was estimated from the absorption intensity at 460 nm. The $[OH^-]$ was estimated from the pH value of each solution. Equilibrium constant

$$K = \frac{[Cr(en)_2(hfacOH)^+]}{[Cr(en)_2(hfac)^{2+}][OH^-]}$$

was calculated as 5.0×10^{10}, 5.5×10^{10} and 6.2×10^{10} M^{-1} for solutions 2, 3 and 4, respectively. The average $K = 5.6 \times 10^{10}$ M^{-1} is significantly larger than the equilibrium constant for the corresponding reaction of the Co(III) analog

$$\frac{[Co(en)_2(hfacOH)^+]}{[Co(en)_2(hfac)^{2+}][OH^-]} = 3.0 \times 10^6 \ M^{-1} \text{ at } 23\ °C \ [3]$$

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